

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
10 October 2002 (10.10.2002)

PCT

(10) International Publication Number  
**WO 02/079340 A1**

(51) International Patent Classification<sup>7</sup>: C09K 3/00,  
C08G 18/00, C07C 271/00

(21) International Application Number: PCT/US02/09648

(22) International Filing Date: 29 March 2002 (29.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/280,728 1 April 2001 (01.04.2001) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,  
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent  
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,  
NE, SN, TD, TG).

**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

D1

(54) Title: RIGID POLYURETHANE FOAMS

(57) Abstract: Polyurethane foams are made using a prepolymer that is the reaction product of an organic polyisocyanate, a hydroxy-functional acrylate or methacrylate, and a polyol. This prepolymer is reacted at specified volume ratios and isocyanate indices with a polyol component that includes at least one polyol. The foam is made in the presence of a blowing agent and catalyst. Preferred blowing agents are water and chemical blowing agents that generate carbon dioxide in the reaction. Preferred catalysts have primary or secondary amine groups that allow them to react into the resulting polymer structure, thus decreasing the level of volatile components.



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In one aspect, this invention is a method of making a rigid polyurethane foam, comprising mixing a polyisocyanate component with a polyol component in the presence of at least one catalyst for the reaction of a polyol or water with a polyisocyanate and subjecting the mixture to conditions sufficient to cause it to  
5 cure to form a polyurethane foam having a bulk density of 45 pounds per cubic foot ( $720 \text{ kg/m}^3$ ) or less, wherein

- (a) the polyisocyanate component contains an isocyanate-terminated prepolymer made by reacting an excess of an organic polyisocyanate with (i) at least one polyol and (ii) at least one hydroxy-functional acrylate or methacrylate,
- 10 (b) the polyol component containing an effective amount of a blowing agent and isocyanate-reactive materials that have an average functionality of at least 2.3 and include at least one polyol and,
- (c) the volume ratio of the polyisocyanate component to the polyol component is no greater than 10:1, and
- 15 (d) the ratio of isocyanate groups in the polyisocyanate component to the number of isocyanate-reactive groups in the polyol component is from 0.8:1 to 1.5:1.

In a second aspect, this invention is an isocyanate-terminated prepolymer which is the reaction product of an excess of an organic polyisocyanate with (i) at least one polyol and (ii) at least one hydroxy-functional acrylate or methacrylate.

20 In a third aspect, this invention is a reactive system comprising

- (a) a polyisocyanate component that contains an isocyanate-terminated prepolymer made by reacting an excess of an organic polyisocyanate with (i) at least one polyol and (ii) at least one hydroxy-functional acrylate or methacrylate,
- 25 (b) a polyol component containing an effective amount of a blowing agent and isocyanate-reactive materials that have an average functionality of at least 2.3 and include at least one polyol,

wherein the system is further characterized by

- (c) a volume ratio of polyisocyanate component to polyol component of no greater  
30 than 10:1,
- (d) a ratio of isocyanate groups in the polyisocyanate component to isocyanate-reactive groups in the polyol component from 0.8:1 to 1.5:1 and
- (e) at least one of the polyisocyanate component or the polyol component containing a catalyst for the reaction of an isocyanate with a polyol or water.

MDI. Especially suitable polymeric MDI products have a free MDI content of from 5 to 40% by weight, more preferably 10 to 25% by weight, and have an average functionality (number of isocyanate groups per molecule) of 2.7 to 4.0, more preferably 2.8 to 3.4. Such polymeric MDI products are available from The  
5 Dow Chemical Company under the trade name PAPI®.

Hydroxy-functional acrylates and methacrylates contain an acrylate ( $\text{CH}_2=\text{CH}-\text{C}(\text{O})-$ ) or methacrylate ( $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{O})-$ ) group and an isocyanate-reactive hydroxyl group. Suitable hydroxy-functional acrylates and methacrylates include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (HEMA), 2-  
10 hydroxylpropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxy-n-butyl acrylate, 2-hydroxy-n-butyl acrylate, 2-hydroxy-n-butyl methacrylate, 4-hydroxy-n-butyl methacrylate, poly(oxyethylene)- and/or poly(oxypropylene)- esters of acrylic or methacrylic acid, wherein the number of oxyethylene and/or oxypropylene groups is preferably from 2 to 10, and the like. Of the foregoing, the  
15 methacrylates are preferred, especially when the polyol component contains primary amine compounds. HEMA is especially preferred.

The polyol(s) used in making the isocyanate-terminated prepolymer has an average at least 2, 2 to 6, especially 2 to 3 and even more especially 2 to 2.5 hydroxyl groups per molecule (functionality). The equivalent weight per hydroxyl  
20 group can vary widely, so long as the prepolymer has the desired equivalent weight. The equivalent weight of each polyol may range from 31 to 1500 or more, but is preferably below 500, more preferably below 300 and even more preferably 200 or below.

Suitable polyols for use in making the isocyanate-terminated prepolymer  
25 include compounds such as alkylene glycols (e.g., ethylene glycol, propylene glycol, 1,4-butane diol, 1,6-hexanediol and the like), glycol ethers (such as diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol and the like), glycerine, trimethylolpropane, tertiary amine-containing polyols such as triethanolamine, triisopropanolamine, and ethylene oxide and/or propylene oxide  
30 adducts of ethylene diamine, toluene diamine and the like, polyether polyols, polyester polyols, and the like. Among the suitable polyether polyols are polymers of alkylene oxides such as ethylene oxide, propylene oxide and 1,2-butylen oxide or mixtures of such alkylene oxides. Preferred polyethers are polypropylene oxides or polymers of a mixture of propylene oxide and a small amount (up to 12 weight

initiators that promote the polymerization of the acrylate and/or methacrylate groups.

A catalyst may be and preferably is used in making the prepolymer. Suitable catalysts include those described by U.S. Pat. No. 4,390,645.

- 5 Representative catalysts include: (a) tertiary amines, such as trimethylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-dimethylethanolamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N-dimethylpiperazine, 1,4-diazobicyclo-2,2,2-octane, bis(dimethylaminoethyl)ether, bis(2-dimethylaminoethyl) ether, morpholine, 4,4'-
- 10 (oxydi-2,1-ethanediyl)bis and triethylenediamine;
- (b) tertiary phosphines, such as trialkylphosphines and dialkylbenzylphosphines;
- (c) chelates of various metals, such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate and the like with metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co
- 15 and Ni;
- (d) acidic metal salts of strong acids, such as ferric chloride, stannic chloride, stannous chloride, antimony trichloride, bismuth nitrate and bismuth chloride;
- (e) strong bases, such as alkali and alkaline earth metal hydroxides, alkoxides and phenoxides;
- 20 (f) alcoholates and phenolates of various metals, such as  $Ti(OR)_4$ ,  $Sn(OR)_4$  and  $Al(OR)_3$ , wherein R is alkyl or aryl, and the reaction products of the alcoholates with carboxylic acids, beta-diketones and 2-(N,N-dialkylamino)alcohols;
- (g) salts of organic acids with a variety of metals, such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni and Cu including, for example, sodium
- 25 acetate, stannous octoate, stannous oleate, lead octoate, metallic driers, such as manganese and cobalt naphthenate; and
- (h) organometallic derivatives of tetravalent tin, trivalent and pentavalent As, Sb and Bi and metal carbonyls of iron and cobalt.

Catalysts are typically used in small amounts. For example, the total

30 amount of catalyst used in making the prepolymer composition may be 0.0015 to 5, preferably from 0.01 to 1 percent by weight.

The isocyanate component may contain a plasticizer. The plasticizer may also be added after the prepolymer is made, or may be present during its formation. A plasticizer may perform several functions, such as reducing the

35 prepolymer viscosity so it is easier to process and handle, modifying the rate of the

The isocyanate component also preferably contains less than 25%, more preferably less than 12%, especially 10% by weight or less of monomeric diisocyanates. By "monomeric diisocyanates", it is meant isocyanate compounds that do not contain urethane, urea, biuret or carbodiimide linkages, that have a molecular weight of 300 or less or which are otherwise formed in the reaction of two or more isocyanate-containing compounds. Having such a low monomeric diisocyanate content substantially reduces the risks of polyisocyanate inhalation exposure, so costly engineering controls such as downdraft ventilation can be substantially reduced or potentially eliminated.

The polyol component includes (i) a polyol or mixture of polyols and (ii) an effective amount of a blowing agent. The polyol component will most typically include a blend of two or more different polyols. The functionality (average number of isocyanate-reactive groups/molecule) of the polyol component (including polyols and amine-functional compounds as described below, but exclusive of non-isocyanate reactive materials, reactive catalysts as described below and water, if present) is at least 2.3.

Suitable polyols are compounds having at least two isocyanate-reactive hydroxyl groups per molecule, provided that the polyol component has an average functionality of at least 2.3, preferably at least 2.5, to 6.0, preferably to 4.0. The functionality of the individual polyols preferably ranges from 2 to 12, more preferably from 2 to 8. As is discussed more fully below, mixtures of two or more polyols together with other isocyanate-reactive compounds are preferred. The hydroxyl equivalent weight of the individual polyols may range from 31 to 2000 or more. However, the equivalent weight of the polyol component as a whole is selected such that when the ratio of isocyanate groups in the polyisocyanate component to the number of isocyanate-reactive groups in the polyol component is from 0.8:1 to 1.5:1, the volume ratio of polyisocyanate to polyol component is no greater than 10:1. Preferably, the hydroxyl equivalent weight of the individual polyols is from 31 to 500, more preferably from 31 to 250, even more preferably from 31 to 200.

Among the suitable polyols are those described above with respect to the isocyanate-terminated prepolymer.

It is preferred that the polyol component includes at least a small amount of a tertiary amine-containing polyol and/or an amine-functional compound. The presence of these materials tends to increase the reactivity of the polyol

weight of the polyol) of poly(ethylene oxide). The high equivalent weight polyol may contain dispersed polymer particles. These materials are commercially known and are commonly referred to as "polymer polyols" (or, sometimes "copolymer polyols"). The dispersed polymer particles may be, for example, polymers of a vinyl monomer (such as styrene, acrylonitrile or styrene-acrylonitrile particles), polyurea particles or polyurethane particles. Polymer or copolymer polyols containing from 2 to 50% or more by weight dispersed polymer particles are suitable. When used, this polymer or copolymer polyol may constitute up to 45%, preferably from 5 to 40%, of the weight of all isocyanate-reactive materials in the polyol component.

The polyol component also contains a blowing agent. Although physical blowing agents such as fluorocarbons, hydrofluorocarbons, chlorocarbons, chlorofluorocarbons and hydrochlorofluorocarbons can be used, the preferred blowing agents are chemical blowing agents that produce carbon dioxide during the foaming reaction. Among these chemical blowing agents are materials such as formate-blocked amines and water. The formate-blocked amines decompose under the foaming conditions to produce carbon dioxide. Water reacts with the polyisocyanate to form carbon dioxide gas that causes the reaction mixture to expand. The blowing agent is used in an amount sufficient to provide the foam with the aforementioned densities. When water is used as the blowing agent, 0.5 to 10, preferably from 3 to 8 parts by weight are used per 100 parts of polyol component.

Some preferred polyol mixtures for use in the polyol component include:

- A. A mixture of a 2-3 functional non-amine-initiated polyether polyol of equivalent weight 200-500 as a main component, a 4-8 functional non-amine-initiated polyether polyol of equivalent weight of 250 or below, and an amine-initiated polyether polyol of equivalent weight of 200 or below. This may optionally contain up to 10 weight percent (based on the total weight of the polyol component) of an amine-functional compound. The amine-functional compound is preferably an amine-terminated polyether.
- B. A mixture of an amine-initiated polyether polyol of equivalent weight of 200 or below as a main component, up to 10 weight percent (based on the total weight of the polyol component) of an amine-functional compound, and at least one 2-3 functional non-amine-initiated

In addition, the polyol component and/or the prepolymer component can contain various auxiliary components as may be useful in making a rigid foam, such as surfactants, fillers, colorants, odor masks, flame retardants, biocides, antioxidants, UV stabilizers, antistatic agents, thixotropic agents and cell  
5 openers.

Suitable surfactants include commercially available polysiloxane/polyether copolymers such as Tegostab (trademark of Goldschmidt Chemical Corp.) B-8462 and B-8404, and DC-198 and DC-5043 surfactants, available from Dow Corning.

Examples of suitable flame retardants include phosphorous compounds,  
10 halogen-containing compounds and melamine.

Examples of fillers and pigments include calcium carbonate, titanium dioxide, iron oxide, chromium oxide, azo/diazo dyes, phthalocyanines, dioxazines and carbon black.

Examples of UV stabilizers include hydroxybenzotriazoles, zinc dibutyl  
15 thiocarbamate, 2,6-ditertiarybutyl catechol, hydroxybenzophenones, hindered amines and phosphites.

Examples of cell openers include silicon-based antifoamers, waxes, finely divided solids, liquid perfluorocarbons, paraffin oils and long chain fatty acids.

The foregoing additives are generally used in small amounts, such as from  
20 0.01 percent to 1 percent by weight of the polyisocyanate component.

Foam according to the invention is prepared by mixing the polyol and polyisocyanate components and allowing the reactants to react and form a foam. Although this invention is not limited to any theory, it is believed that as the prepolymer reacts with the polyol component, the heat that is released causes the  
25 acrylate and/or methacrylate groups to polymerize, thus forming bridges between the prepolymer molecules and contributing to the overall network of the polymer in the cured foam. An advantage of this invention is that the reaction proceeds rapidly when the components are mixed at ambient to moderately elevated temperatures, such as from 20 to 70°C, preferably from 35-65°C. This simplifies  
30 handling and applying the foam. Another advantage of the invention is that because of the low volume ratios of the polyol and isocyanate components, a variety of commonly available mixing and dispensing equipment can be used. In the applications of particular interest, the mixed isocyanate and polyol components are dispensed onto a part or assemblage where localized  
35 reinforcement, corrosion protection, sound insulation or vibration dampening is

Component	Parts by Weight	Equivalent Weight	Functionality
HEMA	4.5	131	1
400 MW Poly(propylene oxide)	5.5	200	2
Polymeric MDI	56.5	141	3.2
Plasticizer (Jayflex™L9P)	32.475	--	0
Organosilicone Surfactant (SPI 202, from SPI Products)	1.0	--	Surfactant
Benzoyl Chloride	0.025	--	Stabilizer

The resulting plasticized Prepolymer Component A has a % NCO of 14.24 weight percent, an equivalent weight of 295, a degree of polymerization of 1.55, a  $M_n$  of 597 and an average functionality of 3.04 isocyanate groups/molecule.

#### B. Polyol Components A and A1

- 5 Polyol Component A is made by mixing the following components:

Component	Parts by Weight	Equivalent Weight	Functionality
Sucrose-Initiated Poly (PO) polyol (Voranol 280, Dow Chemical)	12.6	200.35	7
Formic acid-blocked amine catalyst (DABCO 8154, from Air Products)	10	112	Catalyst and chemical blowing agent
Polyether polyol (PG 76-120, from Arch Chemicals)	67.350	467.5	3
Reactive amine catalyst (DABCO T, from Air Products)	8.5	146	--

### C. Preparation of Foam Example 1

Foam is prepared by dispensing Prepolymer Component A and Polyol Component A at a 4:1 volume ratio on a Gusmer foaming machine at a dispensing pressure of 450-700 psi (2760-4825 kPa), and allowing to cure at room temperature. Both components are preheated to 130-160°F (54-71°C) to reduce the viscosity and obtain better mixing. A foam having a density well below 45 pounds per cubic foot (720 kg/m<sup>3</sup>) is obtained.

### D. Preparation of Foam Example 1A

Foam Example 1A is made from Prepolymer Component A and Polyol Component 1A using the same general method as described in part C. Tack free time is around 10 seconds and density is 6.5 pounds/cubic foot (104 kg/m<sup>3</sup>). The foam modulus (ASTM 1621D) is between 2000 and 3000 psi (13,800-20,700 kPa). Flow rate is about 60 g/s.

### Examples 2 and 2A

#### A. Preparation of Prepolymer Component B

Prepolymer Component B is made in the same general manner as Prepolymer Component A, using the following ingredients:

Component	Parts by Weight	Equivalent Weight	Functionality
HEMA	5.96	131	1
400 MW Poly(propylene oxide)	5.416	200	2
Polymeric MDI	53.624	141	3.2
Plasticizer (Platinol™79P)	35	--	0

The resulting plasticized Prepolymer Component B has a % NCO of 12.93 weight percent, an equivalent weight of 325, a degree of polymerization of 1.69, a  $M_n$  of 617 (exclusive of plasticizer) and an average functionality of 2.92 isocyanate groups/molecule (exclusive of plasticizer).

Polyol Component B1 is prepared by mixing the following components:

Component	Parts by Weight	Equivalent Weight	Functionality
Polyether Polyol (PG 76-120)	21	467.5	3
Primary Amine-Terminated Polyether (DA400, from Huntsman)	5	200	2
Reactive Amine Catalyst (DABCO T)	12	146	--
Ethylene diamine-initiated poly (PO) polyol (Voranol 391, from Dow Chemical)	48	143.5	4
Reactive Amine Catalyst (Polycat™15)	5	187	1
Organosilicone Surfactant (Tegostab B-8404)	2	--	--
Water	7	9	--

#### C. Preparation of Foam Samples 2 and 2A

5      Foam Example 2 is prepared by mixing Prepolymer Component B and Polyol Component B in the general manner described in Example 1. Modulus and stress (ASTM D1621D) are 192 psi (1325 kPa) and 11 psi (76 kPa), respectively. Core density is 2.23 pounds/cubic foot (36.8 kg/m<sup>3</sup>).

10      Foam Example 2A is prepared by mixing Prepolymer Component B and Polyol Component B1 in the general manner described in Example 1. The density of the foam is below 45 pounds per cubic foot (720 kg/m<sup>3</sup>).

N,N,N'-trimethyl-N'-hydroxyethyl bis(aminoethyl) ether (ZF-10, from Huntsman)	9.5	190	--
Dimethyl-1,2-(2-aminoethoxy)ethanol	3	133	--
Organosilicone Surfactant (Tegostab B-8404)	3	--	--
Water	7.7	9	--

### C. Foam Preparation

Foam Example 3 is prepared by mixing Prepolymer Component C and Polyol Component C in the general manner described in Example 1. The resulting  
5 foam has a density of below 45 pounds per cubic foot (720 kg/m<sup>3</sup>).

10. The prepolymer of claim 8 wherein the organic polyisocyanate is MDI or a polymeric MDI.
11. The prepolymer of claim 10 wherein the hydroxy-functional acrylate or methacrylate is hydroxyethyl methacrylate.
12. A reactive system comprising
  - (a) a polyisocyanate component that contains an isocyanate-terminated prepolymer made by reacting an excess of an organic polyisocyanate with (i) at least one polyol and (ii) at least one hydroxy-functional acrylate or methacrylate,
  - (b) a polyol component containing an effective amount of a blowing agent and isocyanate-reactive materials that have an average functionality of at least 2.3 and include at least one polyol and,wherein the system is further characterized by
  - (i) a volume ratio of polyisocyanate component to polyol component of no greater than 10:1,
  - (ii) a ratio of isocyanate groups in the polyisocyanate component to isocyanate-reactive groups in the polyol component from 0.8:1 to 1.5:1 and
  - (iii) at least one of the polyisocyanate component or the polyol component containing a catalyst for the reaction of an isocyanate with a polyol or water.
13. The reactive system of claim 12 wherein the volume ratio of polyisocyanate component to polyol component is 1:1.5 to 6:1.
14. The reactive system of claim 13 wherein the hydroxy-functional acrylate or methacrylate is a methacrylate.
15. The reactive system of claim 14 wherein the hydroxy-functional acrylate or methacrylate is hydroxyethyl methacrylate.
16. The reactive system of claim 12 wherein at least one polyol in the polyol component contains a tertiary amine group.
17. The reactive system of claim 12 wherein the catalyst includes a reactive amine catalyst.
18. The reactive system of claim 12 wherein the blowing agent is water or a chemical blowing agent that releases CO<sub>2</sub>.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/09648

## Continuation of B. FIELDS SEARCHED Item 3:

CAS ONLINE

search terms: foam, polyisocyanate, ?acrylate, polyol, amine, MDI